

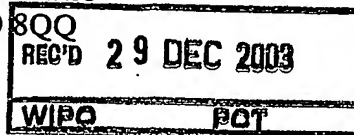


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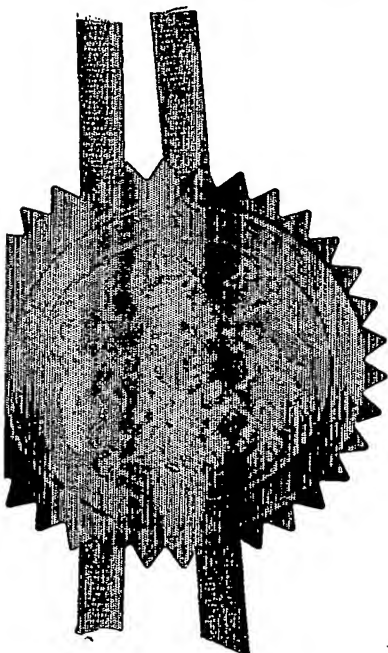
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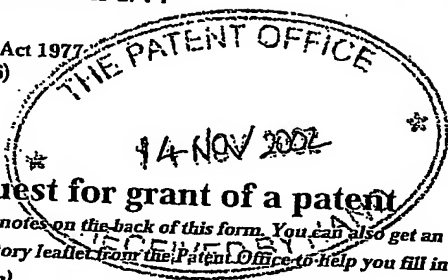
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7882871004
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Description 14

Claim(s) 6

Abstract

Drawing(s) 3 *23*

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DUPLICATE

Method for Producing Carbon Nanotubes and/or Nanofibres

The present invention relates to a method of producing
5 carbon nanotubes and/or nanofibres, and to nanotubes and/or
nanofibres so produced.

Carbon nanotubes are tubular fullerenic structures which may
be single-walled or multi-walled. Carbon nanofibres are
10 fullerenic nanostructures in which the graphitic layers are
not tubular: for example, solid fullerenic cylinders or
hollow cylindrical fullerenic structures wherein the
fullerene net is not parallel to the cylinder axis.

15 Carbon nanotubes and nanofibres have remarkable mechanical
and electrical properties and are being investigated for
many potential applications. These materials have been
produced previously by using various approaches, including
laser or arc-discharge ablation of a carbon/catalyst mixture
20 target. The materials are usually produced in an entangled
state.

For larger scale synthesis, the most promising methods have
been based on chemical vapour decomposition (CVD). In these
25 methods, a carbon containing gas is decomposed at high
temperature under the influence of a finely divided
transition metal catalyst.

Large quantities of multi-walled nanotubes can be grown
30 using CVD by methods well known in the literature (H.G.
Tennant, US 5,165,909). However, this material, sometimes
termed 'cotton candy', is highly entangled, a characteristic

that reduces its utility in certain applications (for example, this material is not readily dispersible as a filler). In addition, nanotubes grown in this way do not have a clearly defined length and often have to be broken up into shorter sections using aggressive chemical treatments (e.g. boiling in concentrated nitric acid) in order to achieve a good dispersion (Shaffer). Particulate substrates have also been used as catalyst supports for growing entangled nanotubes (e.g. WO00/17102).

WO00/73205 discloses a method for producing carbon nanotubes from carbon monoxide gas using silica-supported cobalt and molybdenum as a catalyst. The single-walled nanotubes produced are locally roughly aligned in bundles but each nanotube travels between different bundles and the material is thus entangled.

Multi-walled nanotubes have also been grown on non-particulate substrates (usually quartz plates or furnace tubes with diameters between 15 mm and 100 mm) in order to form aligned arrays, also known as 'carpets', 'forests', or 'grass' (e.g. Andrews). The process usually involves the thermal decomposition of ferrocene/toluene mixtures at 600-1000 °C although a variety of related feedstocks may be used. By varying processing parameters such as time, temperature, and catalyst concentration it is possible to adjust the length, diameter, and packing density of the nanotubes formed within certain ranges (e.g. Singh).

Aligned nanotubes have also widely been prepared on flat substrates by using various types of plasma enhancement (for example microwave, radio-frequency or direct current) (e.g. Ren). Aligned nanotubes grown by thermal CVD often have a

higher crystalline quality than their 'cotton candy' counterparts.

5 The present invention provides in a first aspect a method
for producing aligned carbon nanotubes and/or nanofibres
comprising providing finely divided substrate particles
having substantially smooth faces with radii of curvature of
more than 1 μm and of length and breadth between 1 μm and 5
mm having a catalyst material on their surface and a carbon-
10 containing gas at a temperature and pressure at which the
carbon-containing gas will react to form carbon when in the
presence of the supported catalyst, and forming aligned
nanotubes and/or nanofibres by the carbon-forming reaction.

15 At the nanometer scale (less than 100 nm), the surface may
have a texture or roughness that stabilises metal catalyst
clusters of suitable sizes for nanotube and/or nanofibre
growth. The surface should be smooth over the order of size
of catalyst material clusters.

20 Preferably, the faces have radii of curvature of more than
10 μm . More preferably, the substantially smooth faces are
substantially flat.

25 Preferably, the catalyst material is dispersed in clusters
on the surface of the substrate particles. More preferably,
the catalyst material clusters are from 0.5 nm to 100 nm in
dimension. Highly preferably, the catalyst material
clusters are from 3 nm to 50 nm in dimension.

30

Optionally, the substrate particles having catalyst material on their surface are prepared by depositing catalyst material on the surface of the substrate particles.

- 5 Metal or metal salts may be introduced onto the substrate particles by a range of treatments including electroless deposition, solvent drying, supercritical drying, sputtering, physical vapour deposition, or electroplating. Subsequent thermal and/or oxidising or reducing gas
- 10 treatments may be used in converting a given salt to a metal or to a suitable precursor for thermal decomposition (see below). Continuous films may be broken up on thermal treatment to form suitable catalyst particles by a dewetting process.

- 15 Alternatively, the substrate particles having catalyst material on their surface may be prepared by providing finely divided substrate particles and a catalyst precursor material and decomposing the catalyst precursor material to
- 20 form the catalyst material in the presence of the substrate particles such that the catalyst material is deposited on the substrate particles. In a preferred embodiment of the invention, the catalyst precursor material is decomposed while the substrate particles are in contact with the
- 25 carbon-containing gas, for example within the main CVD furnace.

- As a further alternative, the substrate particles having catalyst material on their surface may be prepared by
- 30 providing finely divided substrate particles of a material that is decomposable to form catalyst material on the surface of non-catalyst substrate particles and decomposing

said material. Some perovskites are known to behave in this way (e.g. Liang).

Preferably, the length and breadth of the substrate particle
5 faces are between 10 μm and 500 μm . If the particle is
facetted, the majority of facets are preferably more than 25
 μm^2 in area and most preferably wider than 2 μm in each
direction.

10 The substrate may be, by way of example, ceramic (silica or
alumina), mineral (mica), metallic (titanium), salt (sodium
chloride, magnesium oxide, calcium oxide) or carbon-based.
The substrate particles may be of graphite, aluminium or
titanium. Preferably, the substrate particles are of silica,
15 carbon, magnesium oxide, calcium oxide, or sodium chloride.
In the most straightforward case, the substrate particles
are simply finely ground powders, such as silica or alumina,
or drawn aluminosilicate fibres, or processed minerals such
as mica. Other materials may be generated by a range of
20 methods, known to those skilled in the art, such as
colloidal processing, spray-drying, hydrothermal processing,
ball-milling extrusion and so on. Freshly prepared materials
with uncontaminated surfaces (e.g. as obtained by prompt use
of ball milled silica, milled using silica-based balls) are
25 preferably used in order to obtain best results.
Preferably, the materials are used within a day of
preparation.

Preferably, the substrate particles are anisotropic in order
30 to provide a large surface area to volume ratio. More
preferably, the substrate particles have one dimension

larger than the other two dimensions or the substrate particles have one dimension smaller than the other two dimensions.

- 5 Optionally, the substrates are coated with a buffer layer. The buffer layer on the surface of the substrate particles serves either to support or enhance the catalyst particles or to isolate the growth process from the underlying material. As an example, such an approach could be useful
- 10 when using a substrate that is convenient to remove after the growth reaction but which has a relatively high solubility for the catalyst metal (such as a magnesium oxide/nickel system). Such a buffer layer may be introduced by deliberate treatment (Sun) or may arise naturally (e.g.
- 15 the oxide layer on titanium particles).

- Preferably, the catalyst material is a transition metal, an alloy of two or more thereof, a compound of a transition metal or a mixture of two or more compounds of transition
- 20 metals. Particularly suitable are the Group VIB chromium (Cr), molybdenum (Mo), tungsten (W) or Group VIIIB transition metals, e. g., iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) or mixtures thereof.
- 25 Metals from the lanthanide and actinide series may also be used. More preferably, the transition metal is iron, cobalt, molybdenum or nickel or mixtures thereof.

- Preferably, the catalyst precursor is a transition metal
- 30 carbonyl, or a transition metal cyclopentadienyl compound. More preferably, the catalyst precursor is ferrocene, nickelocene, cobaltocene, iron pentacarbonyl or nickel

tetracarbonyl. The catalyst precursor compound may provide the carbon-containing gas, for example where ferrocene is used to provide iron catalyst and cyclopentadiene carbon-containing gas.

5

Preferably, the carbon containing gas is carbon monoxide, an oxygen containing organic compound or a hydrocarbon, or a mixture of two or more thereof. More preferably, the carbon containing gas is carbon monoxide, benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene, methane, ethane, propane, hexane, ethylene, propylene, acetylene, formaldehyde, acetaldehyde, acetone, methanol, ethanol or a mixture of two or more thereof. In preferred embodiments, the carbon-containing compound is toluene, xylene or benzene. It is of course only required that the reactant be gaseous under the reaction conditions.

Optionally, one or more boron and/or nitrogen containing compound is provided in addition to the carbon containing gas. It has been shown in flat substrate studies that boron or nitrogen can be introduced into the carbon lattice (Terrones), by using boron or nitrogen containing species in the feedstock for the CVD reaction. Accordingly, it is possible to grow large volumes of such 'doped' materials using this invention by the addition of suitable species, such as ammonia, pyridine, aniline, borazine, borane, phthalocyanines, to the feedstock.

Optionally, one or more promoter compounds is provided in addition to the carbon containing gas. Promoters aid the catalytic selectivity or reactivity. These agents may be added as the catalyst is formed or during growth of the

nanotubes and/or nanofibres. For example, thiophene may be added to encourage the production of herringbone fibres or single-walled nanotubes (Singh, Zhu).

5 Optionally, a diluent gas is provided mixed with the carbon containing gas. The diluent is preferably an inert gas, e.g. argon. The carbon-containing gas may also be mixed with non carbon-containing gases that play no direct role in the carbon-forming reaction but which play a contributory role, 10 for instance by reacting with amorphous carbon as it is formed (as a by-product) and so keeping the reaction sites on the catalyst clean and available for nanotube formation. Gases which may be mixed with the carbon-containing gas include argon, hydrogen, nitrogen, ammonia, or helium.

15

The substrate particles may be introduced into the CVD reactor batchwise, or added to the furnace continuously either using standard powder handling techniques or by carrying in a suitable gas (see PCT/GB02/02239). Preferably, 20 substrate particles are provided and product particles are removed from a reaction vessel in a continuous fashion. Once introduced to the furnace, the substrate particles may sit in a fixed bed, a fluidised bed, or be carried within the gas flows in the system.

25

Preferably, the method described above further comprises the step of recovering the aligned nanotubes and/or nanofibres.

Preferably, gaseous effluent from the reaction is recycled 30 with or without clean up.

Suitably, formation of the nanotubes and/or nanofibres takes place at a temperature of from 650 °C to 1250 °C, e.g. 650 °C to 850 °C. Preferred gas pressures are from 0.1 to 50 bar A, preferably from 0.5 to 5 bar A, more preferably 1 to 2 bar A. The ratio of catalyst metal to carbon fed to the reaction zone is preferably less than 1:100, e.g. 1:100 to 1:500.

In a second aspect, the invention relates to finely divided substrate particles having substantially smooth faces with radii of curvature of more than 1 µm and of length and breadth between 1 µm and 5 mm with a catalyst material on the surface of the substrate particles and with aligned carbon nanotubes and/or nanofibres on the surface of the substrate particles. The nanotube and/or nanofibre coated substrate particles may be used directly (with either or both components contributing to a desired active or passive functionality).

Alternatively, the nanotubes or nanofibres may be removed from the substrate by dissolution of the substrate (e.g. hydrogen fluoride treatment of silica, or hydrothermal treatment of sodium chloride) or by dissolution of the catalyst or buffer layers (e.g. iron in dilute hydrochloric acid). The now disconnected nanotubes and/or nanofibres and substrates may be conveniently separated by filtration or sedimentation. In particular the disconnected materials may be placed in a medium of intermediate density such that the substrate particles sink and the nanotubes and/or nanofibres rise (or vice versa). After separation, the substrate particles may be reused.

In a third aspect, the invention relates to nanotubes and/or nanofibres produced by a method as described above.

Preferably, the nanotubes and/or nanofibres are separated
5 from the substrate particles by partial or complete
dissolution of the substrate particles or catalyst
materials.

The invention will be further described with reference to
10 the following Example and with reference to the Figures, in
which:

Figure 1 shows an SEM image of aligned nanotubes grown on
quartz substrate at ~ 700 °C for 90 minutes.

15 Figure 2 shows a Raman spectrum taken from the nanotubes
grown at 700 °C taken using a 514 nm excitation laser.

Figure 3 shows TGA on nanotubes grown at 700 °C for 90
minutes, 750 ml min⁻¹ Ar:H₂ flow rate and at a feed rate 1.2
20 ml hr⁻¹ of the solution.

Example

A solution containing 2 wt% of ferrocene dissolved into
25 toluene was prepared. 100 mg of high surface area quartz
powder was prepared by ball milling. Milling time was 2
hours using alumina ball-bearings. The silica broke up into
flakes approximately 10 to 40 µm in diameter and around 1 µm
thick. The ground silica was sorted with a 75 µm sieve. The
30 fine powder was then placed into a horizontal tube furnace

(internal diameter 14 mm, length 90 cm) and heated to 700 °C. The solution was sprayed into the furnace at 1.2 ml hr⁻¹ using a dry argon-hydrogen atmosphere for 90 minutes. The ratio of argon to hydrogen was 14:1 with a total gas flow rate of 750 ml min⁻¹. The products were characterised by electron microscopy, both scanning (SEM) and high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy and Thermogravimetric analysis (TGA). From Figure 1 it can be seen that the nanotubes are in abundance, high purity, and aligned with constant lengths. The nanotubes are mainly in the bundled form growing perpendicular to the surface of the support. The average diameters of the nanotubes were 27 ± 2.7 nm determined using TEM.

In Figure 2 the quality of the material based upon the relative intensity of the peak at ~ 1350 cm⁻¹ to ~ 1580 cm⁻¹ indicates that the nanotubes contain few defects. TGA (Figure 3) indicates that approximately 40 % of the weight loss was due to the nanotubes. The remaining powder was iron oxide supported on quartz. The average weight loss from TGA was ~ 32.5 %.

The advantages of the technique of the Example for large scale production of carbon nanotubes are summarised as follows:

1. Low production cost: the raw materials involved for forming the support, catalyst and carbon feedstock are cheap and readily available in large quantities.

2. The method results in high volumes and high yield of good quality pure nanotubes, and can readily be scaled up to an industrial level.

3. Characteristics such as nanotube/nanofibre diameter and length can be manipulated by the growth process.

The disadvantage of known flat substrate methods of production compared with the method of the Example is that the ratio between the growing surface area and volume of support is low as a result of the geometry of the plates. Because the growth is confined to a macroscopic surface the total volumetric yield of product is low.

The disadvantage of the method of W000/73205 compared with the method of the Example is that aligned, non-entangled nanotubes are not produced. This is apparently because the substrate particles used in that method do not have the required characteristics.

Whilst the applicants do not wish to be bound by this theory, it is believed that during growth the aligned nanotube or nanofibre arrays grow from all sides of the substrate particle, leading to a large volume of carbon product. During growth the substrate particles move apart in order to accommodate the growing nanotubes.

References:

- Andrews, R., Jacques, D., Rao, A.M., Derbyshire, F., Qian, D., Fan, X., Dickey, E.C., and Chen, J., *Continuous*
5 *production of aligned carbon nanotubes: a step closer to commercial realization*. Chemical Physics Letters, 1999. 303(5-6): p. 467-474.
- Ren, Z.F., Huang, Z.P., Xu, J.W., Wang, J.H., Bush, P.,
10 Siegal, M.P., and Provencio, P.N., *Synthesis of large arrays of well-aligned carbon nanotubes on glass*. Science, 1998. 282(5391): p. 1105-1107.
- Liang, Q., Tang, S.H., Gao, L.Z., Chen, Z.Y., Zhang, B.L.,
15 Yu, Z.L., *A study on production of carbon nanotubes by decomposition of CH₄ over the pre-reduced catalysts LaNiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇ and La₂NiO₄*, Acta Chim. Sin., 2001, 59, 8, p. 1236-1240.
- 20 Sun, X., Stansfield, B., Dodelet, J.P., Desilets, S., *Growth of carbon nanotubes on carbon paper by ohmically heating silane-dispersed catalytic sites*, Chem. Phys. Lett. 363 (2002) 415-421.
- 25 *Production of aligned carbon nanotubes by the CVD injection method*, Singh C, Shaffer M, Kinloch I, and Windle A, Physica B, Vol 323, No. 1-4, 339-340, 2002
- 30 Shaffer MSP, Fan X, Windle AH, *Dispersion and packing of carbon nanotubes*, Carbon, 1998, Vol.36, No.11, 1603-1612

- Terrones, M., Benito, A.M., MantecaDiego, C., Hsu, W.K., Osman, O.I., Hare, J.P., Reid, D.G., Terrones, H., Cheetham, A.K., Prassides, K., Kroto, H.W., and Walton, D.R.M., Pyrolytically grown BxCyNz nanomaterials: Nanofibres and nanotubes. *Chemical Physics Letters*, 1996. 257(5-6): p.576-582.
- 10 Terrones, M., Redlich, P., Grobert, N., Trasobares, S., Hsu, W.K., Terrones, H., Zhu, Y.Q., Hare, J.P., Reeves, C.L., Cheetham, A.K., Ruhle, M., Kroto, H.W., and Walton, D.R.M., Carbon nitride nanocomposites: Formation of aligned CxNy nanofibers. *Advanced Materials*, 1999. 11(8): p. 655
- 15 Singh, C., Quested, T., Boothroyd, C., Thomas, P., Kinlock, I., Abou Kandil, A., Windle, A.H., *Synthesis and characterisation of carbon nanofibres produced by the floating catalyst method*, *J. Phys. Chem. B.*, 2002, 106, p. 10915-10922.
- 20 Zhu, H.W., Xu, C.L., Wu D.H., Wei B.Q., Vajtai R., Ajayan P.M., Direct synthesis of single-walled carbon nanotube strands, *Science*, 2002, 296, 884-886

Claims:

1. A method for producing aligned carbon nanotubes and/or
5 nanofibres comprising providing finely divided
substrate particles having substantially smooth faces
with radii of curvature of more than 1 μm and of length
and breadth between 1 μm and 5 mm and having catalyst
material on their surface and a carbon-containing gas
10 at a temperature and pressure at which the carbon-
containing gas will react to form carbon when in the
presence of the supported catalyst, and forming aligned
nanotubes and/or nanofibres by the carbon-forming
reaction.
- 15 2. A method as claimed in Claim 1, wherein the faces have
radii of curvature of more than 10 μm .
3. A method as claimed in either one of the preceding
20 claims, wherein the substantially smooth faces are
substantially flat.
4. A method as claimed in any one of the preceding claims
wherein the catalyst material is dispersed in clusters
25 on the surface of the substrate particles.
5. A method as claimed in Claim 4, wherein the catalyst
material clusters are from 0.5 nm to 100 nm in
dimension.

6. A method as claimed in Claim 5, wherein the catalyst material clusters are from 3 nm to 50 nm in dimension.

5 7. A method as claimed in any preceding claim, wherein the substrate particles having catalyst material on their surface are prepared by depositing catalyst material on the surface of the substrate particles.

10 8. A method as claimed in Claim 7, wherein the catalyst material is deposited by electroless deposition, solvent drying, supercritical drying, sputtering, physical vapour deposition or electroplating.

15 9. A method as claimed in any one of Claims 1 to 6, wherein the substrate particles having catalyst material on their surface are prepared by providing finely divided substrate particles and a catalyst precursor material and decomposing the catalyst precursor material to form the catalyst material in the
20 presence of the substrate particles such that the catalyst material is deposited on the substrate particles.

25 10. A method as claimed in Claim 9, wherein the catalyst precursor material is decomposed while the substrate particles are in contact with the carbon-containing gas.

30 11. A method as claimed in any one of Claims 1 to 6, wherein the substrate particles having catalyst material on their surface are prepared by providing finely divided substrate particles of a material that is decomposable

to form catalyst material on the surface of non-catalyst substrate particles and decomposing said material.

5 12.A method as claimed in any preceding claim, wherein the length and breadth of the substrate particle faces are between 10 μm and 500 μm .

10 13.A method as claimed in any preceding claim, wherein the substrate particles are of silica, alumina, carbon, mica, magnesium oxide, calcium oxide, sodium chloride, pure metal or aluminosilicate or a mixture of two or more thereof.

15 14.A method as claimed in Claim 13, wherein the substrate particles are of graphite, aluminium or titanium.

15.A method as claimed in any preceding claim, wherein the substrate particles are anisotropic.

20 16.A method as claimed in Claim 15, wherein the substrate particles have one dimension larger than the other two dimensions or wherein the substrate particles have one dimension smaller than the other two dimensions.

25 17.A method as claimed in any one of preceding claims where the substrates are coated with a buffer layer.

18.A method as claimed in any preceding claim, wherein the substrate is freshly prepared.

30

19.A method as claimed in Claim 18, wherein the substrate is prepared by colloidal processing, spray-drying, hydrothermal processing, or ball-milling.

5 20.A method as claimed in any preceding claim, wherein the catalyst material is a transition metal, an alloy of two or more thereof, a compound of a transition metal or a mixture of two or more compounds of transition metals.

10 21.A method as claimed in Claim 20, wherein the transition metal is iron, cobalt, molybdenum or nickel.

22.A method as claimed in Claim 9 or Claim 10, wherein the catalyst precursor is a transition metal carbonyl, or a
15 transition metal cyclopentadienyl compound.

23.A method as claimed in Claim 22, wherein the catalyst precursor is ferrocene, nickelocene, cobaltocene, iron pentacarbonyl or nickel tetracarbonyl.

20 24.A method as claimed in any preceding claim, wherein the carbon containing gas is carbon monoxide, an oxygen containing organic compound or a hydrocarbon, or a mixture of two or more thereof.

25 25.A method as claimed in Claim 24, wherein the carbon containing gas is carbon monoxide, benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene, methane, ethane, propane, hexane, ethylene,
30 propylene, acetylene, formaldehyde, acetaldehyde, acetone, methanol, ethanol or a mixture of two or more thereof.

26. A method as claimed in any one of the preceding claims wherein one or more boron and/or nitrogen containing compound is provided in addition to the carbon containing gas.
27. A method as claimed in any one of the preceding claims, wherein one or more promoter compounds is provided in addition to the carbon containing gas.
28. A method as claimed in Claim 27, wherein the promoter compound is thiophene.
29. A method as claimed in any one of the preceding claims, wherein a diluent gas is provided mixed with the carbon containing gas.
30. A method as claimed in any preceding claim, wherein the substrate particles are reacted within a fluidised bed.
31. A method as claimed in any preceding claim, wherein substrate particles are provided and product particles are removed from a reaction vessel in a continuous fashion.
32. A method as claimed in any preceding claim, further comprising the step of recovering the aligned nanotubes and/or nanofibres.
33. A method as claimed in any one of the preceding claims, wherein gaseous effluent from the reaction is recycled with or without clean up.

34. A method as claimed in any preceding claim, wherein the reaction takes place at a temperature between 650 °C and 1250 °C.

5

35. Finely divided substrate particles having substantially smooth faces with radii of curvature of more than 1 µm and of length and breadth between 1 µm and 5 mm with a catalyst material on the surface of the substrate particles and with aligned carbon nanotubes and/or nanofibres on the surface of the substrate particles.

10

36. Carbon nanotubes and/or nanofibres produced by a method as claimed in any one of the preceding claims.

15

37. Nanotubes and/or nanofibres as claimed in Claim 36, wherein the nanotubes and/or nanofibres are separated from the substrate particles by partial or complete dissolution of the substrate particles or catalyst materials.

20

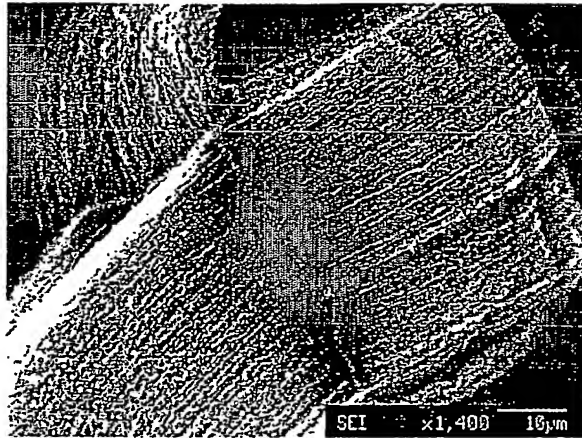


Figure 1

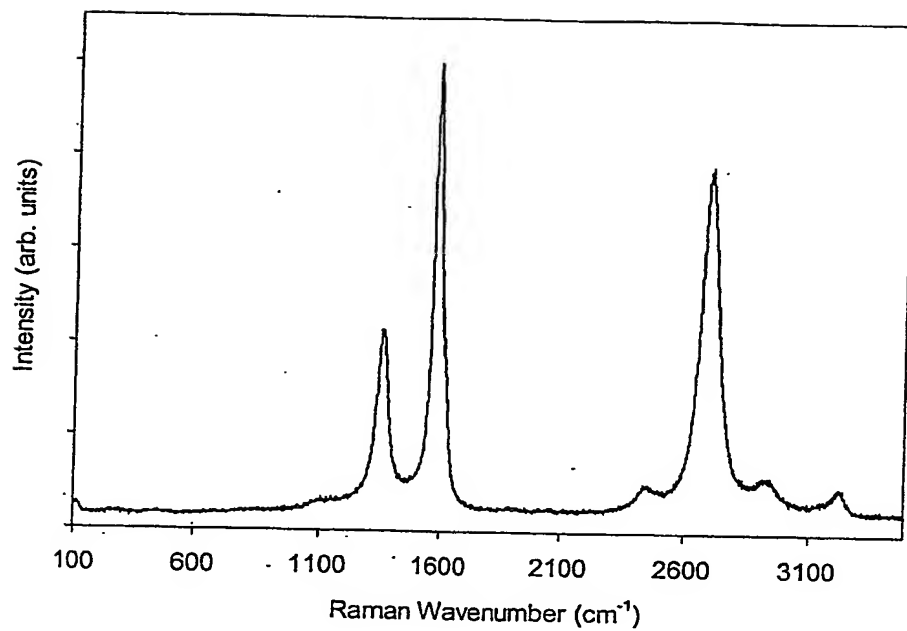


Figure 2

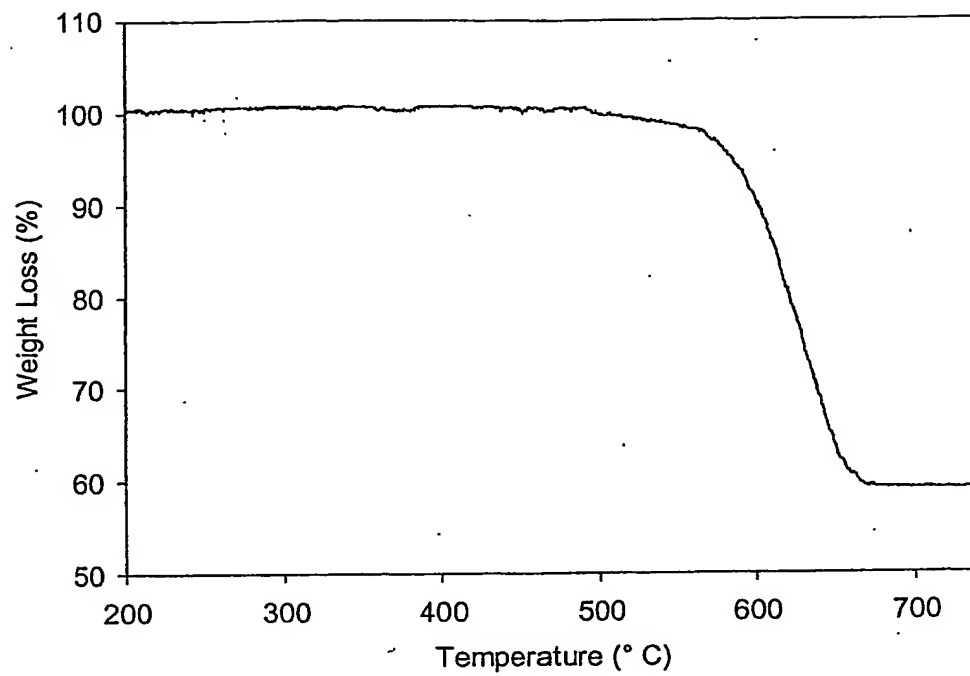


Figure 3

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